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(54) DETERGENT COMPATIBLE FABRIC SOFTENING AND ANTI-STATIC COMPOSITIONS

(71) We, THE PROCTER & GAMBLE COMPANY, a corporation organised under the laws of the State of Ohio, United States of America, of 301 East Sixth Street, Cincinnati, Ohio 45202, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to fabric softening compositions and detergent compositions.

Various clay materials have been utilised in many different types of detergent systems for widely different purposes. Clays, for example, have been disclosed for use as builders (Schwartz and Perry, *Surface Active Agents*, Interscience Publishers, Inc., 1949, pp. 232 and 299); as water-softeners (British Patent 461,221); as anti-caking agents (U.S. Patents 2,625,513 and 2,770,600); as suspending agents (U.S. Patents 2,594,257, 2,594,258 and 2,920,045); and as fillers (U.S. Patent 2,708,185).

It is also well known that some clay materials can be deposited on fabrics to impart softening properties thereto. Such clay deposition is usually realized by contacting fabrics to be so treated with aqueous clay suspensions (see, for example U.S. Patents 3,033,699 and 3,594,221). The copending U.S. patent applications of Storm and Mirschl, Serial No. 271,943, filed July 14, 1972; Ohren, Serial No. 279,127, filed August 9, 1972, Nirschl and Gloss, Serial No. 305,416, filed November 10, 1972; and Glass and Nirschl, Serial No. 305,417, filed November 10, 1972; relate to the use of clays as softeners in laundry compositions.

While clay can provide softening properties, and can do so in the presence of detergent and builder substances used in the cleansing or laundering of fabrics, they do not provide anti-static properties. Commercially-acceptable fabric softener compositions do additionally provide anti-static benefits, and such benefits have come to be expected by the user of such products. Unfortunately, fabrics coated with clays, while exhibiting a soft "hand", tend to develop higher levels of static charge than the uncoated fabrics.

Various quaternary ammonium compounds known in the art possess anti-static properties. These compounds, while suitable in combination with clay materials to provide the anti-static properties which are not provided by the clays, can be inhibited in their provision of anti-static effects by the presence of anionic substances conventionally employed in the cleansing of fabrics in laundering operations.

The fabric softening and anti-static compositions of the present invention have anti-static properties and are capable of providing their effects in the presence of conventional detergent compositions so as to concurrently launder, soften and impart anti-static benefits to fabrics.

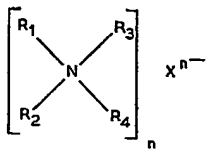
The present invention is based in part upon the discovery that certain acidic materials, and certain substituted amino compounds defined hereinafter, will mitigate the interactive effects of quaternary ammonium anti-static agents and conventional detergent laundering compositions. These materials, termed compatibilizing agents hereinafter, can be employed in combination with quaternary ammonium anti-static agents and clay fabric-soften-

ing materials in fabric-laundering operations to provide treated textile materials with simultaneous cleansing, anti-static and fabric-softening effects.

The present invention provides a fabric softening composition comprising:

(a) from 2% to 90% by weight of smectite-type clay having a particle size below 50 microns and having an ion-exchange capacity of at least 50 meq/100 grams;

(b) from 1% to 40% by weight of water-insoluble quaternary ammonium anti-static agent of the formula:



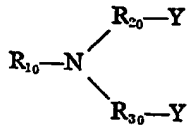
wherein R_1 and R_2 represent hydrocarbyl groups containing from 10 to 22 carbon atoms, R_3 and R_4 represent hydrocarbyl groups containing from 1 to 4 carbon atoms, X is an anion and n is an integer from 1 to 3; and

(c) from 1% to 40% by weight of compatibilizing agent which may be one or more of the following:

i) fatty acid having from 8 to 30 carbon atoms in the alkyl or alkenyl chain;

ii) benzene mono-, di- or tricarboxylic acid containing from 0 to 2 hydroxyl functions; and

iii) substituted amino compounds of the formula:



wherein R_{10} represents an alkyl group containing from 1 to 22 carbon atoms; R_{20} and R_{30} represent alkyl groups containing from 1 to 10 carbon atoms or hydrogen, but not more than one of R_{20} and R_{30} can represent hydrogen; and Y represents $—CONH_2$; $—CON(R_{40})_2$; or —COOH; wherein R_{40} represents an alkyl group containing from 1 to 4 carbon atoms or hydrogen.

Such compositions can be conveniently added to a laundry washing water to which a laundry detergent composition is also added.

The present invention also provides as integral formulations a detergent composition comprising

(A) from 2% to 30% by weight of anionic, nonionic, ampholytic and/or zwitterionic detergent;

(B) from 0% to 60% by weight of organic or inorganic detergent builder salt;

(C) from 1% to 50% by weight of smectite-clay as defined above;

and (D) from 0.5 to 15% by weight of water-insoluble quaternary ammonium antistatic agent, the weight ratio of the smectitie-type clay to the quaternary ammonium anti-static agent being from 40:1 to 1:1;

(E) from 0.5% to 15% by weight of compatibilizing agent as hereinbefore defined.

Such detergent compositions, merely added to water, provide in a single step a laundering bath suitable for simultaneous cleansing, softening and providing anti-static effects to a fabric washed therein.

The invention also provides a method for simultaneously cleansing, softening and reducing static build-up in fabrics which comprises treating the textiles in an aqueous liquor comprising:

(α) from 10 ppm to 3000 ppm of detergent;

(β) from 0 ppm to 6000 ppm of organic or inorganic detergent builder salt;

(γ) from 5 ppm to 5000 ppm of smectite-type clay as defined above;

(δ) from 2.5 to 1500 ppm of water-insoluble quaternary ammonium anti-static agent, the weight ratio of the smectite-type clay to the quaternary ammonium anti-static agent being from 40:1 to 1:1; and

(ε) from 2.5 ppm to 1500 ppm of compatibilizing agent, the weight ratio of the quaternary ammonium anti-static agent to the compatibilizing agent being in the range from 5:1 to 1:5.

The weight ratio of smectitie-type clay to quaternary ammonium compound in the detergent compositions herein is generally from 40:1 to 1:1, and is preferably 10:1 to 3:1.

The quaternary ammonium compound and compatibilizing agent are generally present in releasable combination in the compositions herein and in a weight ratio of quaternary ammonium compound to compatibilizing agent of from about 1:5 to about 5:1. A preferred ratio is from 3:1 to 1:2. The amount of compatiblizing agent in the non-detergent (just softening) compositions is preferably 2% to 20% by weight, while in the detergent compositions it is preferably 1% to 10% by weight.

The detergent compositions herein generally provide a solution pH of from 7 to 12 when dissolved in water at a concentration of 0.12% by weight.

The compositions and method of this invention employ three essential ingredients; the clay softener; the quaternary ammonium anti-static agent; and the compatibilizing agent. The detergent compositions of the invention additionally comprise a water-soluble detergency compound and, usually, a detergency builder salt. The smectitie-type clay

functions to soften the laundered fabrics while the quaternary ammonium compound provides anti-static effects on the fabrics and adds an increment of softening benefits to the fabrics.

The detergent and builder components provide cleansing and building effects. The various components of the compositions herein are described in greater detail hereinafter.

The essential clay component of the present compositions consists of particular smectite clay materials. These smectite clays are present in the fabric softening compositions of this invention at levels from 2% to 90%, preferably 5% to 90%, and most preferably 8% to 75%, by weight. In the detergent compositions of this invention, the smectite clay is used in an amount from 1% to 50%, preferably 5% to 25% by weight. The clays used herein are "impalpable", that is, they have a particle size which cannot be perceived tactilely. Impalpable clays have particle sizes below 50 microns; the clays used herein generally have a particle size range of 5 microns to 50 microns.

The clays can be described as expandable, three-layer clays, i.e. alumino-silicates and magnesium silicates, having an ion exchange capacity of at least 50 meq/100 grammes of clay. The term "expandable" as used to describe clays relates to the ability of the layered clay structure to be swollen, or expanded, on contact with water. The three-layer expandable clays used herein are those materials classified geologically as smectites.

There are two distinct classes of smectite-types clays; in the first, aluminium oxide is present in the silicate crystal lattice, in the second class of smectities, magnesium oxide is present in the silicate crystal lattice. The general formulas of these smectities are $Al_2(Si_2O_5)_2(OH)_2$ and $Mg_3(Si_2O_5)_2(OH)_2$, for the aluminium and magnesium oxide type clay, respectively. It is to be recognised that the range of the water of hydration in these clays can vary with the processing to which the clay has been subjected. This is immaterial to the use of the smectite clays in the present invention in that the expandable characteristics of the hydrated clays are dictated by the silicate lattice structure. Furthermore, atom substitution by iron and magnesium can occur within the crystal lattice of the smectites, while metal cations such as Na+, Ca++, as well as H+, can be co-present in the water of hydration to provide electrical neutrality. Except as noted hereinafter, such cation substitutions are immaterial to the use of the clays herein since the desirable physical properties of the clays are not substantially altered thereby.

The three-layer, expandable alumino-silicates useful herein are further characterized by a dioctahedral crystal lattice, while the expandable three-layer magnesium silicates have a trioctahedral crystal lattice.

As noted hereinabove, the clays employed in the compositions of the instant invention contain cationic counter ions such as protons, sodium ions, potassium ions, calcium ions and magnesium ions. It is customary to distinguish between clays on the basis of one cation predominantly or exclusively absorbed. For example, a sodium clay is one in which the absorbed cation is predominantly sodium. Such absorbed cations can become involved in exchange reactions with cations present in aqueous solutions. A typical exchange reaction involving a smectite-clay is expressed by the following equation:

$$\text{smectite-type clay (Na)} + HN_4OH = \text{smectite-clay } (NH_4) + NaOH$$

Since in the foregoing equilibrium reaction, one equivalent weight of ammonium ion replaces an equivalent weight of sodium, it is customary to measure cation exchange capacity (sometimes termed "base exchange capacity") in terms of milliequivalents per 100 g of clay (Meq/100 g). The cation exchange capacity of clays can be measured in several ways, including by electrodialysis, by exchange with ammonium ion followed by titration or by a methylene blue procedure, all as fully set forth in Grimshaw, "The Chemistry and Physics of Clays", pp. 264—265, Interscience (1971). The cation exchange capacity of a clay mineral relates to such factors as the expandable properties of the clay and the charge of the clay, which, in turn, is determined at least in part by the lattice structure. The ion exchange capacity of clays varies widely in the range from about 2 meq/100 g for kaolinites to about 150 meg/100 g, or more for certain clays of the montmorillonite variety. Illite clays have an ion exchange capacity somewhere in the lower portion of the range, i.e. around 26 meq/100 g for an average illite clay.

It has been determined that illite and kaolinite clays, with their relatively low ion exchange capacities, are not useful in the present compositions. However, smectites, such as nontronite, having an ion exchange capacity of approximately 50 meq/100 g, saponite, which has an ion exchange capacity of around 70 meq/100 g, and montmorillonite, which has an ion exchange capacity greater than 70 meq/100 g, have been found to be useful in the present compositions and they are deposited on the fabrics to provide the desired softening benefits. The clays useful for the present invention can be characterised as expandable, three-layer smectite-type clays having an ion exchange capacity of at least 50 meq/100 g. A smectite-type clay known as "fooler clay", found in a relatively thin vein above the

Black Hills in the U.S.A., has the requisite ion exchange properties characteristic of the clays useful herein and such "fooler clay" is encompassed by the term "smectite-type clay", as used herein.

Smectite clays suitable for use in the compositions of the invention are commercially available. Such clays include, for example, montmorillonite, volchonskoite, nontronite, hectorite, saponite, sauconite, and vermiculite. The clays are available under various tradenames, for example Thixogel #1 (also, "Thixo-Jell") and Gelwhite GP from Georgia Kaolin Co., Elizabeth, New Jersey; Volclay BC and Volclay #325, from American Colloid Co., Skokie, Illinois; Black Hills Bentonite BH450, from International Minerals and Chemicals; and Veegum F, from R. T. Vanderbilt. Such smectite-type minerals obtained under the foregoing tradenames can comprise mixtures of the various mineral entities. Such mixtures of the smectite minerals are suitable for use in the present invention: "Volclay" and "Veegum" are Registered Trade Marks.

While any of the smectite-type clays having a cation exchange capacity of at least 50 meq/100 g are useful herein, certain clays are preferred. For example, Gelwhite GP is an extremely white form of smectite clay and is therefore preferred when formulating white granular detergent compositions. Volclay BC, which is a smectite-type clay mineral containing at least 3% of iron (expressed as Fe_2O_3) in the crystal lattice, and which has a very high ion exchange capacity, is one of the most efficient and effective clays for use in the present compositions and is preferred from the standpoint of product performance. Certain smectite clays marketed under the name "bentonite" are sufficiently contaminated by other silicate minerals for their ion exchange capacity to fall below the requisite range, and such clays are of no use in the present compositions.

Appropriate clay minerals for use herein can be selected by virtue of the fact that smectites exhibit a true 14Å x-ray diffraction pattern. This characteristic pattern, taken in combination with exchange capacity measurements performed in the manner noted above, provides a basis for selecting particular smectite-type minerals for use in the compositions of the invention.

The quaternary ammonium anti-static agents are used in the softening compositions in an amount of 1% to 40%, preferably 2% to 25%, by weight. They are used in the detergent compositions of the invention in an amount of 0.5% to 15%, preferably 1% to 10%, by weight. Whichever composition of the invention is employed in providing an aqueous laundering bath, an amount sufficient to provide a concentration of quaternary ammonium compound in the bath of 2.5 ppm (parts per million) to 1500 ppm. is used. In general, the quternary anti-static agents are used in either type of composition at a clay-to-quaternary weight ratio of from 40:1 to 1:1, preferably from 10:1 to 3:1.

The anti-static agents for use herein have been defined above.

Quaternary ammonium compounds wherein n=1 are commercially available and are preferred herein for this reason.

The quaternary ammonium anti-static agents herein are characterised by being insoluble in water, existing therein in what appears to be the mesomorphic liquid crystalline state. The insolubility of the quaternary salts used herein is a critical aspect of this invention inasmuch as water-soluble quaternary salts become chemically affixed to the surface of the clay. When the quaternary anti-static agent is affixed to the surface of the clay, it does not provide the desired anti-static effects on fabrics.

The quaternary ammonium anti-static agents used in this invention can be prepared in various ways well known in the art. Many such materials are commercially available. The quaternaries are often made from alkyl halide mixtures corresponding to the mixed alkyl chain lengths in fatty acids. For example, the "di-tallow" quaternaries are made from alkyl halides having mixed C_{14}—C_{18} chain lengths. Such mixed di-long chain quaternaries are useful herein and are preferred from a cost standpoint.

Practically any anionic group can be the counter-ion in the quaternary compounds used herein. The anionic groups in the quaternary compounds can be exchanged, one for another, using standard anion exchange resins. Thus, quaternary ammonium salts having any desired anion are readily available. While the nature of such anions has no effect on the compositions and processes of this invention, chloride ion is the preferred counter-ion from a cost standpoint.

The following are representative examples of water-insoluble quaternary ammonium anti-static agents suitable for use in the compositions and processes of the invention. They can all be formulated in releasable combination with the detergent ingredients in detergent compositions. Ditallowdimethylammonium chloride is an especially preferred quaternary anti-static agent for use herein by virtue of its low cost, low solubility and high anti-static activity; other useful di-long chain quaternary compounds are dicetyldimethylammonium chloride; bis-dicosyldimethylammonium chloride; didodecyldimethylammonium chloride; ditallowdimethylammonium bromide; dioleoyldimethylammonium hydroxide; ditallowdiethylammonium chloride; ditallowdipropylammonium bromide; ditallowdibutylammonium fluoride; cetyldecylmethylethylammonium chloride; bis - [ditallowdi-

methylammonium]sulfate; and tris - [di-tallowdimethylammonium] - phosphate.

The compatibilizing agent can be a fatty acid having from 8 to 30 carbon atoms in the alkyl or alkenyl chain. Such acids can therefore be saturated or unsaturated; they can be of straight or branched chain configuration. Examples of this class of fatty acids include caprylic acid, perlargonic acid, capric acid, undecanoic acid, lauric acid, tridecanoic acid, myristic acid, palmitic acid, stearic acid, oleic acid, linoleic acid, arachdic acid, behenic acid, lignoceric acid and cerotic acid.

Preferred are fatty acids having from 12 to 20 carbon atoms. Examples of these preferred acids include lauric acid, myristic acid, palmitic acid, oleic acid, stearic acid and arachidic acid. These acids can be of synthetic or natural origin. Examples of synthesis and recovering processes are well known in the art.

Alternative compatibilizing agents are the benzene mono-, di- and tricarboxylic acids having from 0 to 2 hydroxyl functions. Examples of such acids are benzoic acid, salicylic acid, phthalic acid and benzene tricarboxylic acid. Particularly preferred is salicylic acid.

Alternative compatibilizing agents are substituted amino compounds defined above.

Preferred herein because of ready availability and also by virtue of its high antistatic activity is N - coco - beta - aminopropionic acid.

Other useful compatibilizing agents include:

Octadecylamino - propionic acid
Methylamino - bispropionamide
Tallow alkyl - amino - dipropionic acid
Dodecylamino - diacetic acid
Hexadecylamino - bisacetamide
Hexylamino - bisbutyramide
N - hexyldecyl - alpha - aminoacetic acid
Dodecyl - aminodiacetic acid
N - octyl - beta - amino acetamide
Butylamino - perlargonamide
Ethylamino - dicaproamide
Methylamino - di - n - heptylamide

The preferred amount of the detergent ingredient in the detergent compositions of the invention is from 5% to 20% by weight. Examples or organic detergents of suitable types are described in U.S. patent 3,579,454 at column 11, line 45 to column 19, line 64.

Preferred for use herein are the alkyl benzene sulfonates, in which the alkyl group contains from 9 to 20 carbon atoms in straight chain or branched-chain configuration, e.g. those of the type described in U.S. patents 2,220,099 and 2,477,383 (especially valuable are linear straight chain alkyl benzene sulfonates in which the average of the alkyl groups is about 11.8 carbon atoms, commonly abbreviated as $C_{11.8}$LAS). Suitable cations include alkali metals (sodium, potassium, lithium) ammonium and substituted ammonium (mono-, di- and tri-ethanol and methanol amines).

Another group of preferred detergents for use herein are the alkyl ether sulfates having the formula $RO(C_2H_4O)_xSO_3M$ wherein R is alkyl or alkenyl of 10 to 20 carbon atoms, x is 1 to 30, and M is a water-soluble cation such as alkali metal, ammonium or substituted ammonium. Such alkyl ether sulfates may be condensation products of ethylene oxide and monohydric alcohols having 10 to 20 carbon atoms. Preferably, R has 14 to 18 carbon atoms. The alcohols can be derived from natural fats, e.g. coconut oil or tallow, or can be synthetic. Lauryl alcohol and straight chain alcohols derived from tallow are preferred herein. Such alcohols may be reacted with 1 to 30, and especially 1 to 6, molar proportions of ethylene oxide and the resulting mixture of molecular species, having, for example, an average of 3 moles of ethylene oxide per mole of alcohol, may be sulfated and neutralized.

Specific examples of suitable alkyl ether sulfates are sodium coconut alkyl ethylene glycol ether sulfate; sodium tallow alkyl triethylene glycol ether sulfate; and sodium tallow alkyl hexaoxyethylene sulfate.

Another group of preferred detergents for use herein are the olefin sulfonates having 12 to 24 carbon atoms. The term "olefin sulfonates" is used herein to mean compounds which can be produced by the sulfonation of α-olefins by means of uncomplexed sulfur trioxide, followed by neutralisation of the acid reaction mixture in conditions such that any sultones which have been formed in the reaction are hydrolysed to give the corresponding hydroxy-alkane-sulfonates. The sulfur trioxide can be liquid or gaseous, and is usually, but not necessarily, diluted by inert diluents, for example by liquid SO_3 or chlorinated hydrocarbons when it is used in the liquid form, or by air, nitrogen or gaseous SO_2 when it is used in the gaseous form.

The α-olefins from which the olefin sulfonates are derived are mono-olefins having 12 to 24 carbon atoms, preferably 14 to 16 carbon atoms. Preferably, they are straight chain olefins. Examples of suitable 1-olefins include 1-dodecene, 1-tetradecene; 1-hexadecene; 1-octadecene; 1-eicosene and 1-tetracosene.

In addition to the true alkene sulfonates and a content of hydroxy-alkanesulfonates, the olefin sulfonates can contain minor amouts of other materials, such as alkene disulfonates, depending upon the reaction conditions, the proportion of reactants, the nature of the starting olefins and the impurities in the olefin

stock and side reactions during the sulfonation process.

A specific anionic detergent which has been found excellent for use herein is described more fully in U.S. Patent 3,332,880.

The detergent compositions of the present invention contain, as a preferred component, an organic or inorganic detergent builder salt. These are normally alkaline, polyvalent anionic substances. In the present composition these water-soluble alkaline builder salts generally serve to maintain the pH of the laundry solution in the range of from 7 to 12, preferably 8 to 11. Furthermore, these builder salts enhance the fabric cleaning performance of the overall compositions while at the same time they serve to suspend particulate soil released from the surface of the fabrics and prevent its redeposition on the fabric surfaces. Surprisingly, although the detergency builder salts serve to suspend clay soils of the kaolinite and illite types and prevent their redeposition on fabrics, they do not appear to interfere with the deposition on fabric surfaces of the smectite-type clay softeners used herein. Furthermore, these poly-anionic builder salts have been found to cause the smectite-type clays present in the granular detergent formulations of the invention to be readily and homogeneously dispersed throughout the aqueous laundering medium with a minimum of agitation. The homogeneity of the clay dispersion is very desirable for the clay to function effectively as a fabric softener, while the ready dispersability allows granular detergent compositions to be formulated.

Suitable detergent builder salts useful herein can be of poly-valent inorganic and poly-valent organic types, or mixtures thereof. Examples of suitable inorganic builder salts include the alkali metal carbonates, borates, phosphates, polyphosphates, tripolyphosphates, bicarbonates, silicates and sulfates. Specific examples of such salts include the sodium and potassium tetraborates, perborates, bicarbonates, carbonates, tripolyphosphates, orthophosphates and hexametaphosphates.

Examples of suitable organic builder salts include (1) water-soluble amino polyacetates, e.g. sodium and potassium ethylenediaminetetraacetates, nitrilotriacetates and N - (2 - hydroxyethyl)nitrilodiacetates; (2) water-soluble salts of phytic acid, e.g. sodium and potassium phytates; (3) water-soluble polyphosphonates, including sodium, potassium and lithium salts of ethane - 1 - hydroxy - 1,1 - diphosphonic acd or of methylenediphosphonic acid.

Other organic builder salts useful herein include the polycarboxylate materials described in U.S. Patent 2,264,103, including the water-soluble alkali metal salts of mellitic acid. The water-soluble salts of polycarboxylate polymers and copolymers such as are described in U.S. Patent 3,308,067 are also suitable herein. It is to be understood that while the alkali metal salts of the foregoing inorganic and organic poly-valent anionic builder salts are preferred from an economic standpoint, the ammonium and alkanol-ammonium (e.g. triethanolammonium, di ethanolammonium) water-soluble salts of any of the foregoing builder anions are useful herein.

Mixtures of organic and/or inorganic builders can be used. One such mixture of builders is disclosed in Canadian Patent 755,038, i.e. a ternary mixture of sodium tripolyphosphate, trisodium nitrilotriacetate and trisodium ethane - 1 - hydroxy - 1,1 - diphosphonate.

While any of the foregoing alkaline poly-valent builder materials are useful herein, sodium tripolyphosphate, sodium nitrilotriacetate, sodium mellitate, sodium citrate and sodium carbonate are preferred. Sodium tripolyphosphate is especially preferred both because of its detergency builder activity and its ability to homogeneously and quickly disperse the smectite clays throughout aqueous laundry media without interfering with clay deposition on the fabric surface. Sodum tripolyphosphate is also especially effective for suspending illite and kaolinite clay soils and retarding their redeposition on the fabric surface.

The detergent builders preferably form 20% to 50% by weight of the detergent compositions of this invention.

The clay-containing compositions of this invention are generally in granular form. The compositions can be conveniently prepared in standard fashion by mixing the clay with the detergent, builder and other optional ingredients (if used) in a crutcher and spray-drying the resulting mixture to form granules. Following this, the quaternary ammonium anti-static agent and the compatibilizing agent can be sprayed on the granules from a melt. It is important to avoid affixing the quaternary compounds to the surface of the clay by an ion exchange mechanism; accordingly, it is preferable to avoid spraying the detergent granules with an aqueous solution or suspension of the quaternary compound. The ion-exchange problem is avoided by employing a melt of the quaternary compound and at least a portion of the compatibilizing agent to spray the granules.

The compositions may be added to water, or to a detergent bath as the case may be, to provide a laundering liquor. Soiled fabrics are added to the laundering liquor and cleansed in the usual manner. The effective amount of the additive or detergent compositions to be used will depend to some extent on the weight of clothes being laundered and their degree of soiling. Aqueous

laundering baths prepared thereby provide adequate cleaning, softening and anti-static benefits with soiled fabrics, especially cotton and cotton/polyester blends.

It will be appreciated that the method of simultaneously cleansing, softening and reducing static build-up on laundered textiles can be conveniently practiced by providing an aqueous treating liquor in a number of ways. A suitable washing liquor can be prepared by adding, for example, a commercially-available built anionic-based laundry detergent composition into a washing machine at a concentration of about 0.12% and separately, adding a softening non-detergent composition of the invention. Suitable treating liquors will normally contain the various ingredients in the amounts (in ppm) given earlier above.

The softening (non-detergent) and the softening/detergent compositions and the method of the invention are illustrated by the following Examples.

EXAMPLE I

A through-the-wash softening detergent composition is prepared containing the following:

Component	Weight Percent
Anionic surfactant	16.6
Sodium tripolyphosphate	43.3
Sodium silicate	5.8
Sodium sulfate	10.0
Gelwhite GP (smectite)	9.8
Ditallow dimethyl ammonium chloride	2.0
Lauric acid	2.0
Miscellaneous minors	*ca.* 3.5
Moisture	Balance

The "anionic surfactant" had a 1.22:1 ratio of sodium tallow alkyl sulfate:sodium $C_{11.8}$ linear alkyl benzene sulfonate.

The "miscellaneous minors" included brighteners, carboxymethylcellulose, coconut alcohol ethoxylate and perfume.

The composition of Example I, employed at at a concentration of 0.12% by weight in a washing liquor, provides simultaneous cleansing and anti-static effects when employed in the washing cycle of a conventional home laundering process.

Substantially similar detergency, fabric softening, and anti-static benefits are obtained when the lauric acid is replaced by an equivalent amount of N - coco - beta - amino propionic acid; octadecylamino - propionic acid; methylamino - bis - propionamide; tallow alkyl - amino - dipropionic acid; dodecylaminodiacetic acid; hexadecyl - amino - bisacetamide; hexylamino - bis - butyramide; N - hexyldecyl - alpha - aminoacetic acid; dodecyl - aminodiacetic acid; N - octyl - beta - amino acetamide; butylamino - perlargonamide; ethylamino - dicaproamide; methylamino - di - n - heptylamide.

Substantially similar detergency, softening and anti-static benefits are obtained when the anionic surfactant mixture of Example I is replaced by an equivalent amount of: sodium tallow alkyl trioxyethylene ether sulfate; sodium coconut alkyl ethylene glycol ether sulfate; sodium tallow alkylhexaoxyethylene sulfate; olefin sulfonates produced by means of uncomplexed sulfur trioxide sulfonation of 1-dodecene; 1-tetradecene; 1-hexadecene; 1-octadecene; 1-eicosene and 1 - tetracosene and sodium linear didecyl benzene sulfonate.

Substantially similar detergency, softening and anti-static benefits are obtained when the clay softening agent in Example I is replaced by an equivalent amount of volchonskoit, nontronite; nectorite; sauconite; and vermiculite; respectively, all such clays having an ion exchange capacity of at least 50 meq/100 g.

Substantially similar detergency, softening and anti-static benefits are obtained when the clay softening agent in Example I is replaced by ditallowdimethylammonium chloride; ditallowdimethylammonium bromide; ditallowdiethylammonium chloride; dioctadecyldimethylammonium chloride; and ditallowdimethylammonium hydroxide.

EXAMPLE II

Through - the - wash - cycle fabric softener compositions having the following formulas are prepared:

Components	Formula (in parts by weight)			
Sodium bicarbonate	7	13	7	13
Ditallow dimethyl ammonium chloride	8	4	8	4
Lauric acid	4	2	—	—
N - coco - beta - amino propionic acid	—	—	4	2
sodium montmorillonite	21	21	21	21
Extender granules	60	60	60	60

The extender granules have the following composition:

	Parts by weight
Sodium linear dodecyl benzene sulfonate	6
Sodium silicate solids (ratio SiO_2 Na_2O=2.0)	12
Sodium carbonate	12
Sodium sulfate	28
Minors	2

When employed in conjunction with a commercially-available anionic-based built detergent composition in a conventional laundering process, the foregoing softener compositions provide fabric softening and anti-static effects.

The extender granules employed in the composition of Example II are replaced with any inert or compatible filler materials such as sodium sulfate or starch with similar results.

EXAMPLE III

A through-the-wash-cycle fabric - softener composition having the following formula is prepared:

Ingredients	Compositions in Parts by weight
Thixogel # (smectite clay)	10
N - coco - beta - amino-propionic acid	2
Dioctadecyldimethyl-ammonium cloride	2
Detergent base granules	86

The detergent base granules have the following composition:

Ingredients	Parts by weight
Sodium dodecyl linear alkyl benzene sulfonate	14
Sodium tallow alkyl trioxyethylene sulfate	6
Sodium tripolyphosphate	25
Sodium sulfate	23
Silicate solids (ratio SiO_2/Na_3=2.0)	12
Moisture and minor ingredients	Balance to 86

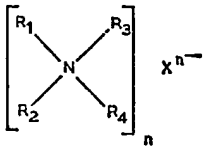
The composition of Example III when used in a conventional laundry operation at a concentration of 0.12% by weight provides fabric-softening, cleansing and anti-static benefits which are substantially similar to what can be obtained from a conventional laundry operation in combination with the subsequent rinse-softening treatment.

WHAT WE CLAIM IS:—

1. A fabric softening composition comprising:

(a) from 2% to 90% by weight of smectite-type clay having a particle size below 50 microns and having an ion-exchange capacity of at least 50 meq/100 grams;

(b) from 1% to 40% by weight of water-insoluble quaternary ammonium anti-static agent of the formula:



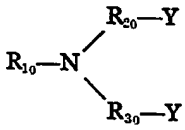
wherein R_1 and R_2 represent hydrocarbyl groups containing from 10 to 22 carbon atoms, R_3 and R_4 represent hydrocarbyl groups containing from 1 to 4 carbon atoms, X is an anion and n is an integer from 1 to 3; and

(c) from 1% to 40% by weight of compatibilizing agent which may be one or more of the following:

i) fatty acid having from 8 to 30 carbon atoms in the alkyl or alkenyl chain;

ii) benzene- mono- di- or tricarboxylic acid containing from 0 to 2 hydroxyl functions; and

iii) substituted amino compound of the formula:



wherein R_{10} represents an alkyl group containing from 1 to 22 carbon atoms; R_{20} and R_{30} represent alkyl groups containing from 1 to 10 carbon atoms or hydrogen, but not more than one of R_{20} and R_{30} can represent hydrogen; and Y represents —$CONH_2$; —$CON(R_{40})_2$; or —COOH; wherein R_{40} represents an alkyl group containing from 1 to 4 carbon atoms or hydrogen.

2. A composition in accordance with Claim 1 comprising 5% to 90% by weight of ingredient (a).

3. A composition in accordance with Claim 2 comprising 8% to 75% by weight of ingredient (a).

4. A composition in accordance with any of Claims 1—3 comprising 2% to 25% by weight of ingredient (b).

5. A composition in accordance with any of Claims 2—4 in which ingredient (c) is (i) the fatty acid or (ii) the benzene derivative.

6. A composition in accordance with Claim 5 comprising 5% to 90% of ingredient (a).

7. A detergent composition comprising

(A) from 2% to 30% by weight of anionic, nonionic, ampholytic and/or zwitterionic detergent;

(B) from 0% to 60% by weight of organic or inorganic detergent builder salt;

(C) from 1% to 50% by weight of smectite-type clay as defined in Claim 1; and

(D) from 0.5% to 15% by weight of water-insoluble quaternary ammonium anti-static agent as defined in Claim 1, the weight ratio of the smectite-type clay to the quaternary ammonium anti-static agent being from 40:1 to 1:1;

(E) from 0.5% to 15% by weight of compatibilizing agent as defined in Claim 1.

8. A detergent composition in accordance with Claim 7 wherein ingredient (A) is anionic detergent.

9. A detergent composition in accordance with Claim 8 wherein the anionic detergent is one or more of the following:

i) water-soluble C_{9-20} linear alkyl benzene sulfonate;

ii) water-soluble alkyl ether sulfate having the formula $RO(C_2H_4O)_xSO_3M$, wherein R is alkyl or alkenyl of 10 to 20 carbon atoms, x is 1 to 30, and M is a water-soluble cation; and

iii) water-soluble olefin sulfonate having 12 to 24 carbon atoms.

10. A detergent composition in accordance with any of Claims 7—9 comprising from 5% to 25% by weight of ingredient (C).

11. A detergent composition in accordance with any of Claims 5—8 comprising from 20% to 50% by weight of ingredient (B).

12. A composition in accordance with any of Claims 7—11 in which ingredient (E) is (i) the fatty acid or (ii) the benzene derivative.

13. A composition according to Claim 1 or 7, substantially as hereinbefore described in or with reference to any of the Examples.

14. A method of simultaneously cleansing, softening and reducing static build-up in laundered textile which comprises treating the textiles in an aqueous liquor comprising:

(α) from 10 ppm to 3000 ppm of detergent as defined in Claim 7;

(β) from 0 ppm to 6000 ppm of organic or inorganic detergent builder salt;

(γ) from 5 ppm to 5000 ppm of smectite-type clay as defined in Claim 1;

(δ) from 2.5 ppm to 1500 ppm of water-insoluble quaternary ammonium anti-static agent as defined in Claim 1; the weight ratio of the smectite-type clay to the quaternary ammonium anti-static agent being from 40:1 to 1:1; and

(ε) from 2.5 ppm to 1500 ppm of compatibilizing agent as defined in Claim 1, the weight ratio of the quaternary ammonium anti-static agent to the compatibilizing agent being in the range from 5:1 to 1:5.

15. A method in accordance with Claim 14 in which ingredient (ε) is (i) the fatty acid or (ii) the benzene derivative.

16. A method in accordance with Claim 14 substantially as hereinbefore described with reference to any of the Examples.

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